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EFFECTS OF ADDED MATERIALS ON SOME PROPERTIES OF HYDRATING PORTLAND CEMENT CLINKERS

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ABSTRACT

Studies were made of the effects of added materials on the properties of a group of portland cement clinkers representing standard-portland, moderate-heat-of-hydration, high-early-strength, sulfate-resistant, and white cements. The materials used were gypsum, sugar, calcium chloride, TDA (grinding aid), tannic acid, triethanolamine, calcium acetate, and fluosilicic acid. The effects were judged by comparing the results of tests of specimens of clinker pastes containing the materials under investigation with the results of similar tests of the clinker pastes to which nothing had been added.

It was found that although some of the materials caused large changes in the behavior of the clinker pastes during their early history, these effects largely disappeared thereafter. Few of the substances had much effect on the results of tests performed at 28 days. No tests were made to evaluate the effect of the added materials after longer periods.

CONTENTS

I. INTRODUCTION

It is known that many properties of hydrating cements are affected differently by various added materials. That this is also true of commerical portland-cement clinkers [1] is shown by recent studies [1] [2] of the aqueous extracts of portland-cement-clinker pastes. The present paper is one of a series dealing with the results of these studies,

[1] To avoid confusion, it is to be noted that "clinker" refers to the ground product containing no added substance, whereas "cement" contains gypsum added during grinding.

[2] Figures in brackets indicate the literature references at the end of this paper.

and is, in part, concerned with the behavior of the pastes from which the filtrates discussed in the preceding paper [1] were removed. The properties investigated were the temperature-time relations and the heats of hydration of the clinker pastes, the strengths of mortar and concrete specimens fabricated from these pastes, the flows of the concretes, the sugar solubilities of the clinkers according to Merriman's procedure [2], and the amounts of floc developed by the clinkers when tested according to Paul's method [3]. The temperature-time curves, the results of the sugar solubility and floc tests, and part of the heats of hydration were determined, using pastes from which no filtrate had been removed.

II. MATERIALS

1. CLINKERS

To facilitate comparisons, the clinkers are given the same identification numbers in this paper as in preceding publications [1, 8]. The chemical analyses and computed compound compositions [4] of the 12 clinkers are given in table 1, together with the finenesses as determined by means of the Wagner turbidimeter [5]. Clinkers 1, 2, 3, 4, 6, 7, 11, and 12 were standard, portland-cement clinkers [6]. Clinker 3, although classified as standard-portland, was actually a high-early-strength-cement clinker, probably because of its greater fineness (2,260 cm²/g, compared to the finenesses of 1,760 to 1,960 cm²/g of the other clinkers). Clinkers 5, 8, and 9 were moderate-heat-of-hydration clinkers, and clinker 10 was a sulfate-resistant cement clinker.

TABLE 1.—*Analyses, calculated compound compositions, and fineness of ground cement clinkers*

Clinker	Chemical composition								Loss on ignition
	SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	Na_2O	K_2O	SO_3	
	%	%	%	%	%	%	%	%	%
1	23.9	5.6	3.4	64.6	0.6	0.56	0.05	0.09	1.1
2	24.9	0.5	4.2	64.1	.9	.04	.25	.00	5.3
3	22.0	2.5	5.7	67.6	1.1	.02	.11	.01	1.1
4	22.3	2.5	5.8	64.0	2.8	.09	1.32	.51	0.9
5	22.8	4.3	5.0	62.8	2.9	.05	1.05	.37	.9
6	22.1	2.5	5.4	64.7	2.6	.62	0.53	.18	1.3
7	21.7	2.2	6.8	65.2	2.7	.18	.18	.32	0.7
8	22.4	4.6	5.0	64.8	2.1	.17	.20	.30	.4
9	22.8	5.3	4.0	64.7	1.4	.87	.09	.35	.5
10	26.0	2.8	2.6	65.8	1.5	.13	.26	.12	.8
11	22.4	2.3	5.9	64.4	3.7	.43	.37	.12	.7
12	21.6	3.9	6.7	64.7	1.3	.12	.76	.28	.8

Clinker	Insoluble residue	Free lime	Calculated compound composition				Fineness
			$3CaO.SiO_2$	$2CaO.SiO_2$	$3CaO.Al_2O_3$	$4CaO.Al_2O_3.Fe_2O_3$	
	%	%	%	%	%	%	cm^2/g
1	0.3	0.1	50	31	0	17	1,760
2	.3	5.3	22	55	10	1	1,960
3	.3	0.7	63	16	11	7	2,260
4	.3	.4	47	29	11	8	1,850
5	.4	.2	42	34	6	13	1,830
6	.2	.9	52	24	10	8	1,780
7	.3	.8	50	25	14	7	1,840
8	.2	1.0	49	27	6	14	1,850
9	.5	0.1	55	24	2	16	1,850
10	.3	.8	45	40	2	9	1,820
11	.5	.4	47	28	12	7	1,910
12	.3	.7	46	27	11	12	1,820

Other characteristics of the clinkers were as follows: Clinker 2 was a white-cement clinker which contained 5.3 percent of free lime and had a loss on ignition of 5.3 percent. Clinkers 4 and 5 were the products of one manufacturer, and clinkers 7 and 8 were the products of another. Each of the remaining clinkers came from a different manufacturer.

Each clinker was ground to the fineness reported in table 1 and stored in an air-tight steel drum.

2. ADDITION AGENTS

The materials added were gypsum, calcium chloride, calcium acetate, sugar (sucrose), tannic acid, triethanolamine, TDA (grinding aid), and fluosilicic acid. The gypsum was a commercial mineral product, ground to pass a No. 200 sieve. Analysis showed that it contained 46.7 percent of SO_3 and had a loss on ignition of 20.1 percent. The TDA was described by its manufacturers as a mixture of "triethanolamine and highly purified soluble salts of modified lignin sulfonic acids." The remainder of the materials were commercial products of chemically pure quality. The quantities used and the methods of incorporating the added materials are shown in table 2.

TABLE 2.—*Addition agents, amounts used, and methods of incorporation*

Material	Amount	Methods of incorporation [a]
	Percent [b]	
Gypsum	3.75	I
Calcium chloride	[c]1.46	II
Calcium acetate	[c]1.35	II
Sugar	0.05	II
Tannic acid	.20	II
Triethanolamine	.10	II
Fluosilicic acid	[c].33	II
TDA	.033	IIA

[a] Methods of incorporation: I, The gypsum was mixed with the clinker for 2 hr in a ball mill with a few pebbles; II, these materials were added to the mixing water; and IIA, the TDA was added to the mixing water for the determinations of the time-temperature curves, the sugar solubilities, and the amounts of floc. For the remainder of the tests, it was dissolved in 7 times its weight of water, sprinkled on the ground clinker, mixed thoroughly in a ball mill, and the mixture allowed to stand for at least 24 hr before use.

[b] The gypsum added was 3.75 percent of the mixture, and the other materials were added in the amounts indicated as percentage by weight of the clinker.

[c] Anhydrous basis.

III. PROCEDURE

1. TEMPERATURE CHANGES OF PASTES

Determinations of the temperature changes of the pastes were made, using mixtures of 200 g of clinker and 70 g of water (C/W ratio=2.86). The pastes, contained in small tin cans, were mixed for 1 min with a high-speed motor-driven stirrer. Copper-constantan thermocouples were inserted in the pastes, and the cans were sealed and placed in stoppered vacuum flasks in a cabinet maintained at 25.0±0.1° C. Frequent measurements of the temperature of the pastes were obtained by connecting the thermocouples to a six-point recording potentiometer. Details of the test and a description of the apparatus have been published [7, 9.]

2. CONDITION OF THE PASTES

Qualitative observations were made of the consistencies of the pastes during mixing and before and after remixing at 2 hr.

3. HEATS OF HYDRATION

Two procedures were used in determining the heats of hydration. The heat evolved at 12 and 24 hr was estimated from the temperature changes of the pastes as described in the following paragraph. The heats of hydration at 7 and 28 days were determined by the heat-of-solution method.

The areas under the curves obtained by plotting the temperatures of the pastes against time were measured with a planimeter for the 12- and 24-hr periods. An average value of 0.0675 cal/hr deg g of cement, determined experimentally, was used to calculate the heat lost from the samples of clinker pastes. To the heat thus removed was added the heat stored in the paste by reason of its elevated temperature. The sum of the heat capacities of the cement and water in the paste was used as the heat capacity of the sample. This value, 0.55 cal/deg g, is somewhat higher than the value 0.41 cal/deg g for a well-aged paste obtained by interpolation of the data of Carlson and Forbrich [10]. No account was taken of the heat capacity of the inside of the vacuum flask and the sample container, since nothing was known of the temperature distribution between the thermocouple and the constant-temperature chamber in which the flask was placed. It was estimated that the heat capacity thus neglected was 0.1 to 0.2 cal/deg g of cement.

In determining the heats of hydration by the heat-of-solution method, the procedure described in Federal Specification SS–C–158a was followed with the exception of the method of preparing the paste samples. Large batches of paste (7,000 g of clinker plus 2,450 g of water, C/W=2.86) were prepared for the filtrations [1, 8] and samples taken as follows: (1) immediately after mixing, (2) from the same batch after filtration at 7 min, (3) after a paste, the duplicate of that filtered at 7 min, had aged for 1 hr 55 min (hereafter designated as 2-hr paste) and had been remixed, (4) after filtration of the 2-hr paste. The C/W ratio of the filtered pastes was restored to 2.86 by the addition of water before the samples were taken. The paste samples were stored in sealed vials at 21° C and tested at 7 and 28 days.

In most of the tests the heat of solution of the dry mixture of the clinker and the added material could not be determined directly. Consequently, it was calculated in all tests. The heats of solution and the losses on ignition were determined separately, both for the clinkers and for the materials investigated. Then for each mixture the contribution of each component to the heat of solution and to the residue on ignition was calculated. The ratio of total heat of solution to the total residue was then calculated and taken as the heat of solution of the mixture on an ignited basis. The heat of hydration of the hydrated paste was determined by subtracting its heat of solution from the value thus obtained.

4. STRENGTH TESTS

The specimens for the strength tests were fabricated by adding aggregates and water to portions of the filtered paste remaining after

the heat-of-hydration samples had been taken. No test pieces were made from unfiltered pastes. After fabrication, all specimens were stored at 21° C for at least 24 hr in a damp closet having a relative humidity of about 95 percent, and then in water at 21° C until tested. The specimens which had no strength at 24 hr were kept in the damp closet for 3 days. The strengths were determined at 1, 3, 7, and 28 days.

The tensile strengths were determined on briquets fabricated from mortar obtained by adding sufficient standard Ottawa sand (20 to 30 mesh) and water to a portion of the paste to give a 1:3 cement-sand mix having a C/W ratio of 2.40.

Compressive strengths were determined on 2-in. cubes made from (a) the same mortar mixture that was used for the briquets and, (b) a concrete mix. The latter was a 1:3½:3½ cement:fine aggregate: coarse aggregate mix with a C/W ratio of 1.25 by weight, in which 20 percent of the fine testing sand (Federal Specification SS–C–158a, paragraph F–4m (1)) was replaced by finely ground potter's flint. The coarse aggregate was the portion of Potomac River gravel passing the ⅜-in. sieve and retained on the No. 4.

The strength specimens were fabricated by a single operator. The concrete specimens were made first, followed in order by the briquets and the mortar cubes. This procedure resulted in the elapse of considerable time between the preparation of the pastes and the fabrication of the briquets and mortar cubes. The pastes were either ½ or 2½ hr old when received by the operator. Many of the pastes were rather stiff, and the test pieces could not be fabricated properly. For this reason, the most reliable results are those obtained for concretes made of the ½-hr pastes.

5. FLOWS (CONSISTENCIES)

The consistencies of the concrete mixtures were obtained according to the procedure given in Federal Specification SS–C–158a, paragraph F–4m (4).

6. MERRIMAN SUGAR SOLUBILITIES

The sugar solubilities were determined according to Merriman's procedure for cements [2] as follows: Fifteen g of clinker and 100 ml of a 15-percent sucrose solution were mixed mechanically for 2 hr. The mixture was then filtered, and 25 ml of the filtrate was titrated with 0.5 N HCl. The "end point" was shown by the color change of phenolphthalein, and the "clear point," if the solution was turbid, was obtained by the further addition of acid until turbidity disappeared.

7. PAUL FLOC TESTS

The amounts of floc developed were determined according to Paul's procedure [3] as follows: One gram of ground clinker was mixed with 100 ml of distilled water in a Nessler tube, and the tube was stoppered and placed in a horizontal position. The relative amount of flocculent precipitate ("none," "small," etc.) at 7 days was observed and recorded. The precipitate was then filtered off, ignited, and weighed. The amount of floc was reported as a percentage of the total weight of clinker originally taken.

IV. RESULTS AND DISCUSSION

1. TEMPERATURE-TIME CURVES, CONDITION OF THE PASTES, AND FLOWS

The temperature changes of the pastes, their observed condition during the first 2 hr, and the flows of the concretes all help to portray the behavior of the hydrating clinkers during their early history, and are therefore grouped together in the discussion.

Figure 1 presents the temperature changes with time of the pastes, with and without additions, during 24 hr or more after mixing. Figure 2 shows, on an enlarged scale, the temperature changes occurring during the first 3 hr. The effects of the various materials are indicated by alteration of the temperatures attained 15 min after mixing the pastes and by changes of the maximum temperatures attained, as well as the times at which they occurred.

In table 3 are listed qualitative observations of the condition of the clinker pastes at various times. The consistency of the concretes, presented as percentage flow in table 4, may also be taken as indicative of the progress of setting, since the pastes from which the specimens were fabricated were about ½ and 2½ hr old at the time the measurements were made.

In the following discussion when the statement is made that a substance changed the behavior of a paste, it is to be understood that the change is in comparison with the behavior of the clinker paste alone. No attempt will be made to discuss the behavior of individual clinkers, since detailed information may better be obtained from the tables and curves. There were occasional or even frequent exceptions to the statements made hereafter, but, in general, the effects of the additions were as described in the following paragraphs.

Gypsum reduced the initial temperatures of the pastes as well as the temperatures attained during the first 3 hr. The maximum temperatures, however, were increased frequently by rather large amounts, and the times required to reach the maximum temperatures were reduced in many instances. The lower temperatures attained during the first 3 hr were accompanied by increases in the fluidities of many of the pastes. Increased flows were observed for the concretes made from many of the clinkers. Certain of the clinkers exhibited quick-setting, which was eliminated by the addition of gypsum.

Sugar increased the temperatures attained in 15 min by nearly all the clinkers, but for many of the clinkers also increased the time required to reach the maximum temperatures. The quick-setting which some of the clinkers exhibited was retained, and this was caused in one case when sugar was added. Sugar also increased the flows of the majority of the concretes.

Calcium chloride caused a decrease in the initial temperatures of seven of the clinker pastes and an increase in the initial temperatures of the remainder. Shortly thereafter, however, the temperatures increased rapidly, and at the end of 3 hr the temperatures of the pastes containing calcium chloride were from 5° to 50° C higher than those of the clinker pastes alone. Calcium chloride eliminated the quick-setting exhibited by five of the clinkers. The flows at ½ hr were increased for nearly all of the clinkers, but at 2½ hr the flows were increased for only four of the clinkers and decreased for all but one of the remainder.

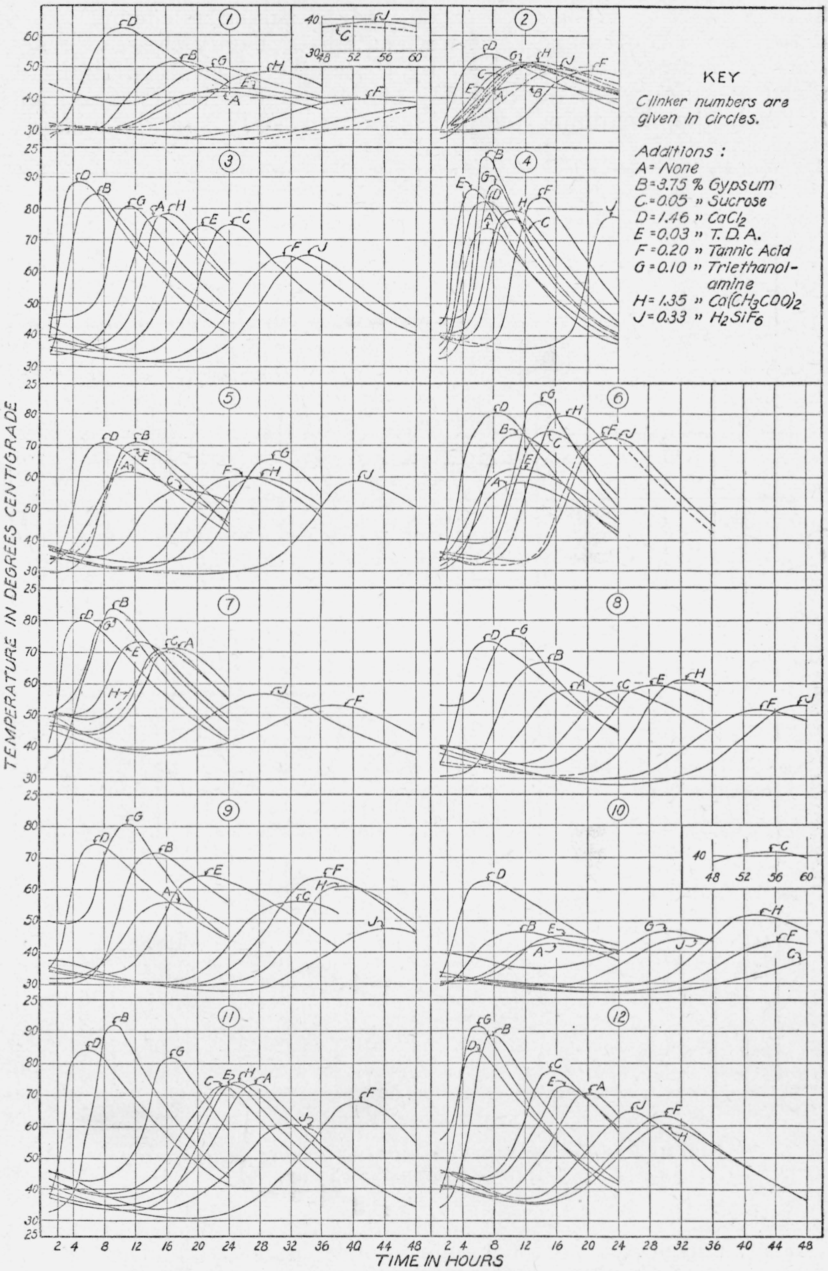

FIGURE 1.—*Temperatures of hydrating clinker pastes.*

TDA increased the temperatures attained at 15 min for nearly all the clinkers. With a few exceptions, the maximum temperatures of the pastes containing TDA were equal to or only slightly greater than the temperatures attained by the clinker pastes containing no added material. For the majority of the clinkers the times required to reach the maximum temperatures were only slightly changed.

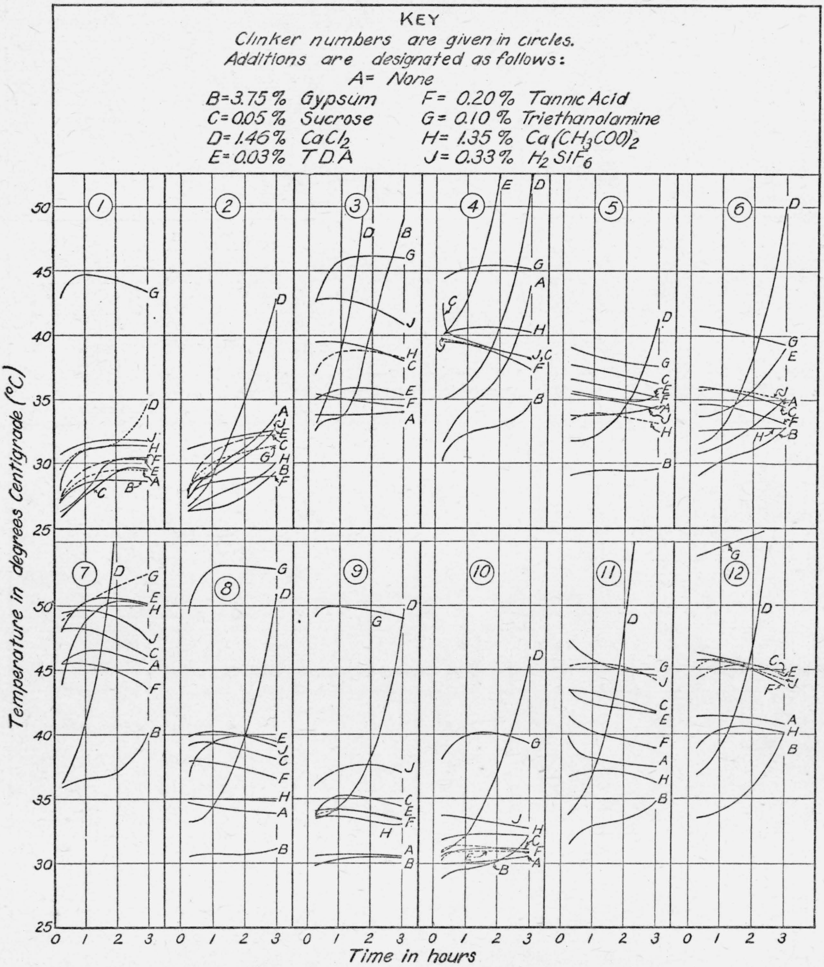

FIGURE 2.—*Temperatures of hydrating clinker pastes during first three hours after mixing.*

TDA eliminated quick-setting and reduced the stiffening of the pastes in most instances. This behavior is also indicated in the data of table 4 where the flows of the concretes containing TDA gave the highest averages both at ½ and 2½ hr. With the exception of the effects on the time-temperature curves, many of these changes may have been caused, at least in part, by prehydration, since the TDA was added to the ground clinkers as an aqueous solution 24 hr before the tests were begun.

TABLE 3.—*Condition of cement clinker pastes at various times with and without added materials*

Clinker	Time	No addition	Gypsum	Sugar	Calcium chloride	TDA	Tannic acid	Triethanolamine	Calcium acetate	Fluosilicic acid
1	During mixing	Fluid	Fluid	Fluid	Fluid	Fluid	Fluid	Fluid	Fluid	Fluid.
	At 2 hr	Soft	Soft	Soft	Stiff	Soft	Soft	Hard [a]	Sticky	Stiff.
	After remixing at 2 hr	Fluid	Plastic	Fluid	Plastic	Fluid	Fluid	Plastic	Fluid	Fluid.
2	During mixing	do	Fluid	do	Fluid	do	do	Fluid	do	Do.
	At 2 hr	Stiff	Soft	Slightly stiff	Slightly stiff	Soft	Stiff	Soft	Soft	Soft.
	After remixing at 2 hr	Plastic	Fluid	Sticky	Plastic	Fluid	Fluid	Fluid	Fluid	Fluid.
3	During mixing	Soft	do	Fluid	Fluid	do	*Quickset*	Quickset	do	Do.
	At 2 hr	Stiff	Hard	Slightly stiff	Hard		Soft	Hard	Stiff	Stiff.
	After remixing at 2 hr	Plastic	Plastic	Fluid	Plastic	Fluid	Fluid	Plastic	Sticky	Fluid.
4	During mixing	Fluid	Fluid	Quickset	Fluid	do	Quickset	Quickset	Soft	*Quickset.*
	At 2 hr	Stiff	Soft	Stiff	Stiff	Soft	Stiff	Hard	Stiff	Hard.
	After remixing at 2 hr	Plastic	Sticky	Plastic	Plastic	Fluid	Plastic	Dry	Sticky	Sticky.
5	During mixing	*Quickset* [b]	Fluid	Quickset	Fluid	do	Quickset	Quickset	Fluid	Quickset.
	At 2 hr	Soft	Soft	Soft	Soft	Soft	Hard	Hard	Soft	Hard.
	After remixing at 2 hr	Sticky	Fluid	Sticky	Fluid	Fluid	Plastic	Plastic	Fluid	Plastic.
6	During mixing	Fluid	do	*Quickset*	do	do	Quickset	Quickset	do	*Quickset.*
	At 2 hr	Slightly stiff	Soft	Slightly stiff	Slightly stiff	Soft	Stiff	Hard	Soft	Hard.
	After remixing at 2 hr	Plastic	Fluid	Soft	Fluid	Fluid	Sticky	Plastic	Fluid	Plastic.
7	During mixing	Quickset	do	Quickset	do	do	Quickset	Quickset	do	Quickset.
	At 2 hr	Hard	Slightly stiff	Hard	Hard	Hard	Hard	Hard	Hard	Hard.
	After remixing at 2 hr	Plastic	Soft	Plastic	Plastic	Soft	Plastic	Dry	Sticky	Plastic.
8	During mixing	*Quickset*	Fluid	*Quickset*	Fluid	Fluid	*Quickset*	Quickset	Fluid	*Quickset.*
	At 2 hr	Slightly stiff	Soft	Slightly stiff	Hard	Slightly stiff	Stiff	Hard	Soft	Stiff.
	After remixing at 2 hr	Plastic	Fluid	Fluid	Fluid	Fluid	Plastic	Dry	Plastic	Plastic.
9	During mixing	Fluid	do	do	do	do	Fluid	Quickset	Fluid	Fluid.
	At 2 hr	Slightly stiff	Soft	Soft	Stiff	Soft	Soft	Hard	Soft	Stiff.
	After remixing at 2 hr	Fluid	Fluid	Fluid	Fluid	Fluid	Fluid	Plastic	Sticky	Fluid.
10	During mixing	do	do	do	do	do	do	Quickset	Fluid	Do.
	At 2 hr	Slightly stiff	Soft	Stiff	Stiff	Soft	Slightly stiff	Stiff	Soft	Soft.
	After remixing at 2 hr	Fluid	Fluid	Fluid	Fluid	Fluid	Fluid	Plastic	Fluid	Fluid.
11	During mixing	*Quickset*	do	Quickset	do	do	Quickset	Quickset	Soft	Quickset.
	At 2 hr	Stiff	Soft	Stiff	Hard	Stiff		Hard	do	Stiff.
	After remixing at 2 hr	Plastic	Plastic	Plastic	Plastic	Fluid	Plastic	Plastic	Sticky	Plastic.
12	During mixing	Quickset	Fluid	Quickset	Fluid	do	Quickset	Quickset	Fluid	Quickset.
	At 2 hr	Hard	Slightly stiff	Hard	Hard	Slightly stiff	Hard		Stiff	Hard.
	After remixing at 2 hr	Plastic	Plastic	Plastic	Plastic	Plastic	Plastic		Sticky	Plastic.

[a] "Hard" in each case indicates that the material could be reworked only by vigorous hammering with a heavy steel tamper.

[b] The condition of the paste designated as "quickset" indicates that vigorous mixing was required to maintain plasticity, that noticeable heat was evolved and that there was a marked decrease in workability. There were different degrees of quick setting. The pastes showing quickset that could be eliminated by mixing without apparent decrease in workability are identified by italic type; no appreciable heat was evolved during the mixing of these pastes.

TABLE 4.—*Flows of concrete mixes with and without added materials at ½ and 2½ hr after initial mixing of cement clinker pastes*

Clinker	Age	No addition	Gypsum	Sugar	Calcium chloride	TDA	Tannic acid	Triethanolamine	Calcium acetate	Fluosilicic acid
	hr	%	%	%	%	%	%	%	%	%
1	½	123	122	134	119	143	127	--------	131	105
	2½	122	111	127	114	132	122	109	116	102
2	½	118	115	110	125	120	90	113	121	105
	2½	--------	113	110	89	103	99	106	109	98
3	½	108	97	109	104	102	97	95	27	87
	2½	103	65	110	66	104	98	84	18	85
4	½	63	93	60	96	114	60	--------	99	60
	2½	54	87	69	54	94	56	43	93	50
5	½	69	114	80	107	121	66	--------	126	48
	2½	79	107	89	110	114	68	58	134	75
6	½	92	99	83	100	112	80	--------	127	81
	2½	79	86	95	85	104	81	68	131	83
7	½	91	97	76	100	94	66	--------	22	64
	2½	81	94	73	69	78	66	--------	--------	--------
8	½	86	104	100	111	108	92	--------	68	87
	2½	85	109	84	100	99	96	87	84	87
9	½	106	99	110	108	115	101	--------	81	111
	2½	101	107	109	90	111	98	89	79	94
10	½	115	111	128	121	113	103	--------	104	115
	2½	107	113	117	104	117	104	118	111	101
11	½	88	94	98	109	112	98	60	35	88
	2½	87	97	98	72	105	98	66	32	89
12	½	78	101	92	111	104	87	--------	37	75
	2½	76	107	87	80	86	74	--------	35	69
Average	½	95	104	98	109	113	89	89	82	86
	2½	89	100	97	86	104	88	83	86	85

Tannic acid increased the temperatures attained in 15 min by all but four of the clinker pastes. The maximum temperatures were increased for only three of the clinkers and were decreased or unchanged for the remainder. The times required to reach the maximum temperatures were increased. All but three of the clinker pastes stiffened more rapidly when tannic acid was used. The majority of the flows were affected only slightly or not at all.

Triethanolamine increased markedly the temperatures reached in 15 min and also increased the maximum temperatures attained. The times required to reach the maximum temperatures were decreased for six of the clinkers and changed only slightly or increased for the remainder. Ten of the clinkers showed quick-setting. The flows of nearly all the concretes were decreased. Two of the clinkers showed little change in the stiffness of the pastes and in the flows of the concretes. In some instances, the flows could not be determined when triethanolamine was added.

Calcium acetate either increased or decreased by a small amount the temperatures attained by the pastes at 15 min. The times required to reach the maximum temperatures were increased. Calcium acetate eliminated the quick-setting exhibited by five of the clinker pastes. In many cases the pastes became very sticky. The flows of the concretes made from six of the clinkers were decreased, whereas the remainder were either increased or not greatly affected.

Fluosilicic acid increased the temperatures attained at 15 min for nearly all the clinkers. The maximum temperatures were decreased for a majority of the clinker pastes, and the times required to reach the maximum temperatures were increased. Quick-setting was retained and, in two instances, was caused by fluosilicic acid. The flows of the concretes made from five of the clinkers were decreased, whereas the remainder were affected only slightly or not at all.

2. HEATS OF HYDRATION

The heats of hydration determined by the heat-of-solution method are given in table 5. Those determined from the time-temperature curves are included in table 6. The treatment of the pastes filtered at 7 min most nearly approximates that of the pastes for which the time-temperature curves were obtained. Accordingly, the heats of hydration at 7 and 28 days of the 7-min pastes sampled before filtration, were made a part of table 6.

It will be noted in table 6 that in 9 out of 108 cases the 1-day heat of hydration equals or exceeds the heat of hydration at 7 days. Each determination is subject to error, and the net effect of individual errors in the two determinations may occasionally cause the 1-day heat of hydration to appear to exceed that at 7 days when this does not actually happen. However, it may well be that the paste at an elevated temperature in the vacuum flask hydrates to a greater extent in 1 day than the corresponding paste, stored at 21° C, hydrates in 7 days.[3] In spite of differences between the two methods, it was felt that the approximate heats of hydration at ½ and 1 day were of sufficient interest to be included in the paper. The heats of hydration at ½, 1, 7, and 28 days have been calculated as percentages of the heat of hydration of the clinker without addition and are presented in table 7 and figure 3. In this manner the direct comparison of heats of hydration measured by different methods is avoided.

For convenience, the level of significance of differences in percentages taken from table 7 was arbitrarily set at 10 percent for the ½- and 1-day and at 5 percent for the 7- and 28-day heats of hydration, respectively. That is, if a material caused a change in the heat of hydration of less than ± 10 percent at ½ and 1 day and ± 5 percent at 7 and 28 days, it is stated in the discussion that no change occurred. Statistical investigation of the heats of hydration shown in table 5 and of other similar data obtained in this laboratory indicates that in these measurements differences of less than 4 cal/g are probably not significant. The reader should bear this in mind in studying table 5 for detailed information on the effects of various additions and the influence of filtration of the pastes at the two ages.

The behavior of the individual cements may be followed in the tables or traced in figure 3. There were occasional exceptions but, in general, the effects of the additions were as described hereafter.

Gypsum increased the heats of hydration at ½ day, sometimes by several hundred percent. At 1 day, two-thirds of the heats of hydration were increased by an average of 30 percent. The changes at 7 days were small, whereas at 28 days most of the heats of hydration were unchanged.

Sugar reduced the heats of hydration of half of the clinkers at ½ day by an average of 48 percent. On the other hand, three heats of hydration were increased by nearly the same amount. At 1 day, one-third of the heats of hydration were decreased by an average of 47 percent, and one-third were increased by about half as much. At 7 and 28 days a few more increases than decreases in the heats of hydration occurred, but the changes were small.

[3] The differences between the 1- and 7-day heats of hydration for the 9 cases were small except when TDA was used. In these two cases the differences may have been caused by the different methods of incorporating the TDA.

TABLE 5.—*Heats of hydration of cement clinker pastes with and without added materials*

Clinker	Age of hydrating paste	Sampled [a]	No addition Filtered at —		Gypsum Filtered at —		Sugar Filtered at —		Calcium chloride Filtered at —		TDA Filtered at —		Tannic acid Filtered at —		Triethanolamine Filtered at —		Calcium acetate Filtered at —		Fluosilicic acid Filtered at —	
			7 min	2 hr	7 min	2 hr	7 min	2 hr	7 min	2 hr	7 min	2 hr	7 min	2 hr	7 min	2 hr	7 min	2 hr	7 min	2 hr
	Days		*cal/g*	*cal/g*	*cal/g*	*cal/g*	*cal/g*	*cal/g*	*cal/g*	*cal/g*	*cal/g*	*cal/g*	*cal/g*	*cal/g*	*cal/g*	*cal/g*	*cal/g*	*cal/g*	*cal/g*	*cal/g*
1	7	Bf	49	49	49	55	49	52	67	59	48	50	47	57	70	76	59	64	58	54
	7	Af	49	50	50	59	50	51	66	59	52	50	50	54	74	71	62	63	58	54
	28	Bf	72	75	73	67	74	74	76	68	73	78	67	75	81	78	87	85	74	72
	28	Af	72	76	69	65	72	74	72	68	68	71	67	75	77	78	85	84	75	72
2	7	Bf	45	47	42	49	48	50	41	43	46	49	41	50	52	56	50	62	60	57
	7	Af	42	43	39	48	43	46	39	39	43	48	41	45	53	53	55	55	57	54
	28	Bf	56	51	58	59	65	69	55	57	66	63	68	65	72	73	69	77	64	64
	28	Af	52	51	59	57	65	69	56	55	61	64	65	64	68	65	69	71	64	63
3	7	Bf	82	81	82	83	84	84	80	77	76	79	78	76	93	96	92	87	84	87
	7	Af	79	79	77	80	82	79	78	80	75	77	77	76	88	89	88	87	86	89
	28	Bf	105	98	107	102	92	100	91	95	99	93	97	100	103	102	105	99	102	101
	28	Af	101	96	96	96	95	99	88	92	96	96	94	94	101	99	102	98	100	100
4	7	Bf	70	66	67	68	79	75	62	65	71	69	75	72	--------	68	83	87	78	77
	7	Af	67	67	67	70	77	72	64	64	69	63	76	73	--------	70	83	82	81	79
	28	Bf	80	80	77	71	83	81	73	74	77	74	80	78	--------	81	89	90	84	82
	28	Af	82	80	77	73	82	81	74	73	71	71	82	80	--------	82	92	95	87	79
5	7	Bf	60	64	65	63	66	67	65	63	58	49	67	69	--------	71	58	67	61	69
	7	Af	63	66	65	62	69	63	66	63	53	52	66	67	--------	73	62	67	65	65
	28	Bf	68	71	69	69	77	73	67	67	70	70	82	80	--------	86	78	78	76	79
	28	Af	70	72	72	70	74	75	67	66	62	73	78	82	--------	87	80	80	83	83
6	7	Bf	53	52	60	59	63	64	66	63	45	52	67	66	--------	71	74	71	67	69
	7	Af	59	55	57	54	59	68	64	62	48	52	68	65	--------	72	77	77	70	71
	28	Bf	74	70	64	68	78	81	70	74	67	65	77	72	--------	79	82	81	79	73
	28	Af	76	73	66	68	81	82	72	71	66	68	79	76	--------	79	83	88	79	75
7	7	Bf	79	82	83	81	78	82	71	70	77	80	79	85	--------		83	90	75	83
	7	Af	86	82	82	79	81	81	71	69	84	82	70	76	--------	--------	82	88	77	84
	28	Bf	89	92	90	92	97	96	89	87	96	92	92	92	--------	--------	99	94	96	97
	28	Af	88	94	88	91	97	97	91	85	97	95	98	97	--------	--------	98	95	96	97
8	7	Bf	61	62	60	57	54	63	64	68	49	55	68	60	--------	77	71	64	60	61
	7	Af	67	60	58	59	62	65	61	67	47	55	66	60	--------	74	69	69	59	62
	28	Bf	75	76	75	71	76	73	78	78	71	70	80	77	--------	87	90	87	78	72
	28	Af	76	77	72	69	78	77	79	77	75	72	82	77	--------	87	93	90	78	80
9	7	Bf	57	54	60	65	50	56	66	64	50	48	63	60	78	75	66	57	54	58
	7	Af	55	55	63	64	57	55	60	63	48	49	63	61	--------	74	68	63	57	60
	28	Bf	74	71	72	69	81	80	70	72	69	68	77	80	84	82	85	82	78	81
	28	Af	74	74	72	73	79	84	72	71	69	70	77	79	--------	82	83	85	81	81
10	7	Bf	41	43	45	45	37	45	53	56	41	46	45	49	61	65	60	58	52	53
	7	Af	45	45	46	49	42	46	54	52	39	40	50	53	--------	66	60	58	50	51
	28	Bf	61	60	61	59	62	62	65	67	60	59	65	66	76	77	72	75	72	70
	28	Af	64	63	61	61	62	66	65	63	57	61	65	64	--------	77	75	75	70	70

11	7	Bf	71	77	76	76	75	78	69	70	65	71	70	73	82	77	72	82	71	76
	7	Af	75	80	74	76	79	80	70	69	68	73	72	74	81	81	78	82	75	77
	28	Bf	89	85	92	88	92	91	79	80	89	93	93	92	95	94	96	97	100	97
	28	Af	90	91	85	89	90	92	77	77	88	91	91	92	97	88	98	97	99	100
12	7	Bf	79	77	78	80	79	82	72	73	76	82	80	80	--------	--------	80	80	83	83
	7	Af	77	77	82	77	80	79	72	69	77	82	79	81	--------	--------	79	79	82	76
	28	Bf	93	92	91	92	88	95	85	88	93	90	91	92	--------	--------	98	98	94	95
	28	Af	95	94	94	93	90	96	89	83	88	92	92	93	--------	--------	102	99	92	95

[a] Bf=Before filtration. Af=After filtration.

TABLE 6.—*Heats of hydration of cement clinker pastes with and without added materials.*[a]

Clinker	Age of hydrating paste	No addition	Gypsum	Sugar	Calcium chloride	TDA	Tannic acid	Triethanolamine	Calcium acetate	Fluosilicic acid
	Days	*cal/g*	*cal/g*	*cal/g*	*cal/g*	*cal/g*	*cal/g*	*cal/g*	*cal/g*	*cal/g*
1	½	9	16	6	39	8	6	20	8	7
	1	27	38	8	51	26	10	43	26	8
	7	49	49	49	67	48	47	70	59	58
	28	72	73	74	76	73	67	81	87	74
2	½	24	19	25	31	26	8	28	24	25
	1	38	31	38	39	39	32	41	41	36
	7	45	42	48	41	46	41	52	50	60
	28	56	58	65	55	66	68	72	69	64
3	½	36	60	14	63	17	11	56	38	15
	1	68	72	63	65	86	24	61	67	24
	7	82	82	84	80	76	78	93	92	84
	28	105	107	92	91	99	97	103	105	102
4	½	48	58	50	57	57	47	58	56	16
	1	53	64	59	63	61	66	64	66	61
	7	70	67	79	62	71	75	--------	83	78
	28	80	77	83	73	77	80	--------	89	84
5	½	38	41	20	48	42	30	14	10	9
	1	54	69	48	59	56	44	32	35	13
	7	60	65	66	65	58	67	--------	58	61
	28	68	69	77	67	70	82	--------	78	76
6	½	35	48	46	58	42	11	52	25	13
	1	48	62	63	65	56	58	67	70	58
	7	53	60	63	66	45	67	--------	74	67
	28	74	64	78	70	67	77	--------	82	79
7	½	34	60	37	58	53	21	61	41	23
	1	69	72	68	66	70	33	70	70	47
	7	79	83	78	71	77	79	--------	83	75
	28	89	90	97	89	96	92	--------	99	96
8	½	21	35	15	51	16	12	57	11	14
	1	49	58	45	64	38	16	67	20	16
	7	61	60	54	64	49	68	--------	71	60
	28	75	75	76	78	71	80	--------	90	78
9	½	24	35	11	51	14	9	60	9	12
	1	45	61	24	63	53	16	68	13	13
	7	57	60	50	66	50	63	78	66	54
	28	74	72	81	70	69	77	84	85	78
10	½	16	23	6	41	15	6	16	8	8
	1	28	36	8	52	33	8	29	11	16
	7	41	45	37	53	41	45	61	60	52
	28	61	61	62	65	60	65	76	72	72
11	½	15	60	21	60	19	14	32	13	18
	1	48	68	66	68	62	19	72	54	35
	7	71	76	75	69	65	70	82	72	71
	28	89	92	92	79	89	93	95	96	100
12	½	23	60	38	60	32	19	62	16	20
	1	63	68	73	69	69	42	68	37	53
	7	79	78	79	72	76	80	--------	80	83
	28	93	91	88	85	93	91	--------	98	94

[a] The ½- and 1-day heats of hydration were determined by integrating the time-temperature curves. The 7- and 28-day heats of hydration are those determined by the heat-of-solution method, using the 7-min. pastes before filtration.

Calcium chloride increased the heats of hydration at ½ day, usually by even larger amounts than did gypsum. At 1 day, three-fourths of the heats of hydration were increased and none were decreased. At 7 days the increases were more frequent and somewhat larger than the decreases, whereas at 28 days half of the heats of hydration were decreased by calcium chloride by an average of 8 percent.

TDA tended to increase the heats of hydration at the early ages and to leave them unchanged or to decrease them later. With a few exceptions the changes were not large.

Tannic acid reduced nearly all the heats of hydration at ½ and 1 day, whereas at 7 and 28 days most of the heats were unchanged or increased. The decreases were frequently rather large, whereas the increases seldom exceeded 25 percent.

TABLE 7.—*Heats of hydration of cement clinker pastes containing added materials as percentages of the heats of hydration of the pastes without addition* [a]

Clinker	Age of hydrating paste	Gypsum	Sugar	Calcium chloride	TDA	Tannic acid	Triethanolamine	Calcium acetate	Fluosilicic acid
	Days	%	%	%	%	%	%	%	%
1	½	178	67	434	89	111	222	89	68
	1	141	30	189	96	37	159	96	30
	7	100	100	136	98	96	143	120	118
	28	101	103	106	101	93	112	121	103
2	½	79	104	129	108	33	117	100	104
	1	82	100	103	103	84	108	108	95
	7	93	107	91	102	91	116	111	133
	28	103	116	98	118	121	128	123	114
3	½	167	39	175	47	31	156	105	42
	1	106	93	96	127	35	90	99	35
	7	100	102	98	93	95	113	112	102
	28	102	88	87	94	92	99	100	97
4	½	121	104	119	119	98	121	117	33
	1	121	111	119	115	124	121	124	115
	7	96	113	89	102	107	----------	119	111
	28	96	104	91	96	100	----------	111	105
5	½	108	53	126	111	79	37	26	24
	1	128	89	110	104	82	59	65	24
	7	108	110	108	97	112	----------	97	102
	28	102	113	99	103	121	----------	115	112
6	½	137	131	166	120	31	159	72	37
	1	129	131	136	117	121	140	146	121
	7	113	119	125	85	126	----------	140	128
	28	87	105	95	90	104	----------	111	107
7	½	177	109	171	156	62	180	121	68
	1	104	99	96	102	48	101	101	68
	7	105	99	90	98	100	----------	105	95
	28	101	109	100	108	103	----------	111	108
8	½	166	71	243	76	57	271	52	67
	1	118	92	130	78	33	137	41	33
	7	98	89	105	80	111	----------	117	98
	28	100	101	104	95	107	----------	120	104
9	½	141	46	212	58	38	250	38	50
	1	136	53	140	118	36	151	29	29
	7	105	88	116	88	110	137	116	95
	28	97	109	95	93	104	114	115	105
10	½	144	38	256	94	38	100	50	50
	1	129	29	186	118	29	104	39	57
	7	110	90	129	100	110	149	146	127
	28	100	102	107	98	107	125	118	118
11	½	400	140	400	127	93	213	86	120
	1	142	137	142	129	40	150	113	73
	7	107	106	97	92	99	116	102	100
	28	103	103	89	100	104	107	108	112
12	½	261	165	261	139	82	27	70	87
	1	108	116	110	110	67	108	59	84
	7	99	100	91	96	101	----------	101	105
	28	98	95	91	100	98	----------	105	101

[a] The ½- and 1-day heats of hydration were determined by integrating the temperature-time curves. The 7- and 28-day heats of hydration were determined by the heat-of-solution method, using the 7-min. pastes before filtration.

Triethanolamine increased most of the heats of hydration at all ages for which data were available. In several instances pastes containing triethanolamine hardened so rapidly that all tests were not performed. The few decreases in the heats of hydration that occurred were usually rather large.

Calcium acetate and fluosilicic acid decreased the majority of the heats of hydration at ½ and 1 day and increased them at 7 and 28 days. In general, the decreases were larger than the increases.

It may be noted that the effects of these substances were frequently large and variable during the first 24 hr, but that by 7 days most of the changes were small. At the end of 28 days very many of the heats of hydration were not affected significantly.

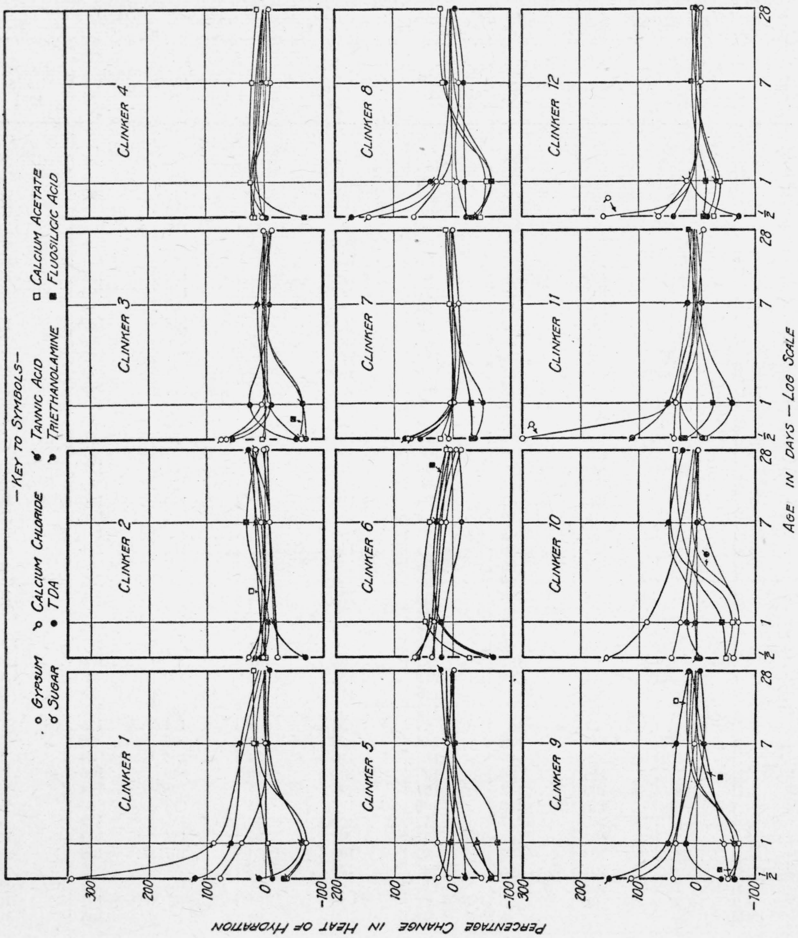

FIGURE 3.—*Effects of addition agents on the heats of hydration of clinker pastes.*

3. STRENGTHS

The results of the strength tests are presented in table 8. Because the 2½-hr pastes were frequently rather stiff, many of the specimens could not be fabricated properly. For this reason the strengths of the ½-hr pastes are the more reliable. The strengths of the specimens made from the ½-hr pastes were calculated as percentages of the strengths of the test pieces containing no added material and are presented in table 8. Few of the pastes containing triethanolamine were workable, and the strengths of specimens containing it are omitted from table 8 and from the discussion.

It should be pointed out that the strength specimens were fabricated from pastes from which part of the added substance had been removed by filtration. Therefore, the amount originally added was not that present during the hardening of the specimens. However, the analyses of the extracted liquids, together with their volumes compared with the amount of water originally added [1], indicated that a large part of the addition remained in the paste.

TABLE 8.—*Strengths of specimens fabricated from filtered [a] pastes with and without additions*

Clinker	Age	Actual tensile strength; no addition	Relative tensile strength [b]							Actual compressive strength; no addition		Relative compressive strength [b]													
			Gypsum	Sugar	Calcium chloride	TDA	Tannic acid	Calcium acetate	Fluosilicic acid	Concrete	Mortar	Gypsum		Sugar		Calcium chloride		TDA		Tannic acid		Calcium acetate		Fluosilicic acid	
												Concrete	Mortar	Concrete	Mortar	Concrete	Mortar	Concrete	Mortar	Concrete	Mortar	Concrete	Mortar	Concrete	Mortar
	Days	*lb/in* [2]	%	%	%	%	%	%	%	*lb/in* [2]	*lb/in* [2]	%	%	%	%	%	%	%	%	%	%	%	%	%	%
1	1	0	(45) [c]	(0)	(90)	(0)	(0)	(40)	(0)	40	80	600	360	0	0	700	950	80	50	0	0	330	150	0	0
	3	110	150	50	240	100	50	220	60	470	900	180	150	50	50	240	270	100	80	90	70	230	260	50	40
	7	255	120	90	130	90	80	130	100	1, 340	2, 380	110	100	80	90	130	170	110	90	100	90	150	170	90	100
	28	375	110	110	110	100	100	110	110	2, 720	4, 520	90	90	100	110	110	120	90	90	100	100	140	150	110	110
2	1	50	180	160	240	200	90	250	140	250	440	110	140	80	110	140	180	110	130	60	60	100	140	80	100
	3	170	120	120	120	120	90	110	130	640	1, 220	120	150	120	160	120	150	120	140	110	110	120	160	130	160
	7	280	100	110	110	110	80	90	110	1, 210	2, 200	100	140	130	160	100	126	120	150	110	100	140	160	150	170
	28	355	140	120	120	130	110	110	110	2, 800	4, 200	90	140	120	160	90	120	110	140	110	100	120	140	140	150
3	1	125	160	0	230	110	0	120	0	460	880	150	140	0	0	250	270	90	90	30	20	50	100	0	0
	3	345	110	100	100	110	80	110	80	2, 020	3, 870	100	80	90	100	110	100	90	90	80	80	100	80	60	80
	7	440	110	100	100	100	90	100	90	3, 150	6, 000	100	90	90	100	100	90	110	100	100	90	100	90	90	100
	28	515	100	100	90	100	100	90	90	4, 640	8, 190	110	90	100	100	100	80	110	100	100	100	90	80	90	110
4	1	100	130	0	210	90	0	90	0	450	650	130	160	0	0	150	170	90	80	0	0	50	90	0	0
	3	230	120	120	150	70	110	130	100	1, 440	1, 690	100	160	90	130	110	140	90	80	80	120	100	210	50	110
	7	260	130	120	150	100	110	130	120	2, 310	2, 460	100	170	110	140	100	140	90	90	100	120	110	210	90	110
	28	345	120	110	120	110	110	130	120	3, 610	3, 410	100	170	100	140	90	120	100	110	110	110	110	190	100	110
5	1	70	210	0	250	80	0	60	0	170	500	280	190	0	0	360	220	170	70	0	0	80	30	0	0
	3	180	150	130	160	90	90	160	110	870	1, 660	130	130	100	120	170	160	110	60	100	60	120	150	50	80
	7	285	120	110	140	80	80	120	90	1. 760	2, 550	110	120	110	140	120	150	110	80	110	90	110	190	90	90
	28	355	130	120	120	100	110	130	90	3, 450	4, 230	100	120	100	120	90	130	100	90	110	70	110	170	100	100
6	1	75	250	0	250	70	0	260	0	300	490	220	270	0	0	240	280	100	80	0	0	160	210	0	0
	3	155	190	160	190	80	130	210	140	1, 210	1, 330	120	200	100	160	150	250	70	80	100	110	140	310	75	140
	7	255	160	130	160	70	100	180	120	2, 130	2, 260	100	170	120	160	120	190	80	80	120	130	150	290	130	150
	28	380	130	110	120	90	100	120	110	3, 460	3, 810	120	150	120	140	100	150	80	90	120	100	130	220	130	120
7	1	35	490	0	630	70	0	50	0	230	410	250	260	0	0	290	350	40	60	0	0	40	60	0	0
	3	200	150	100	150	110	80	90	80	1, 150	1, 380	120	190	80	130	130	200	80	130	60	70	110	130	20	80
	7	250	140	70	140	120	90	100	90	2, 240	2, 370	110	160	90	110	100	180	90	140	80	80	100	120	60	80
	28	235	180	130	190	180	120	140	130	3, 810	2, 990	110	200	90	110	90	180	90	160	80	90	80	120	80	90
8	1	30	320	0	630	0	0	0	0	100	240	420	250	0	0	550	480	0	0	0	0	0	0	0	0
	3	170	110	100	160	90	100	140	60	630	1, 350	160	130	70	110	210	190	130	80	100	90	170	150	10	40
	7	260	100	110	140	80	110	120	120	1, 490	2, 420	100	110	100	130	140	160	110	70	110	110	120	130	90	110
	28	360	120	110	120	100	110	130	120	2, 900	4, 490	110	110	110	130	110	120	110	90	120	110	130	150	120	120

See footnotes at end of table.

TABLE 8.—*Strengths of specimens fabricated from filtered*[a] *pastes with and without additions*—Continued

Clinker	Age	Actual tensile strength; no addition	Relative tensile strength [b]							Actual compressive strength; no addition		Relative compressive strength [b]													
												Gypsum		Sugar		Calcium chloride		TDA		Tannic acid		Calcium acetate		Fluosilicic acid	
			Gypsum	Sugar	Calcium chloride	TDA	Tannic acid	Calcium acetate	Fluosilicic acid	Concrete	Mortar	Concrete	Mortar	Concrete	Mortar	Concrete	Mortar	Concrete	Mortar	Concrete	Mortar	Concrete	Mortar	Concrete	Mortar
	Days	*lb/in*	%	%	%	%	%	%	%	*lb/in*	*lb/in*	%	%	%	%	%	%	%	%	%	%	%	%	%	%
9	1	40	350	0	450	0	0	0	0	150	260	390	310	0	0	410	450	0	0	0	0	0	0	0	0
	3	220	130	0	140	70	50	100	50	1, 020	1, 600	150	140	0	0	160	180	90	60	60	50	80	120	40	50
	7	290	130	100	130	80	100	110	110	1, 970	2, 740	100	110	90	110	120	150	80	70	90	110	110	160	80	100
	28	440	100	80	100	80	90	100	90	3, 500	4, 510	100	100	100	140	100	120	80	80	100	110	100	140	100	120
10	1	0	(85)	(0)	(125)	(40)	(0)	(0)	(0)	0	0	(390)	(400)	(0)	(0)	(440)	(780)	(140)	(110)	(0)	(0)	(0)	(0)	(0)	(0)
	3	140	110	30	170	80	40	100	100	690	860	120	120	60	30	150	220	80	70	60	60	100	110	80	100
	7	195	120	100	170	80	90	130	130	1, 140	1, 520	110	120	100	110	130	190	100	80	90	110	120	170	110	130
	28	365	110	100	120	90	100	120	100	2, 340	3, 180	100	110	110	130	100	140	100	80	100	110	140	180	120	140
11	1	60	230	0	410	50	0	0	0	130	260	370	350	0	0	650	550	100	90	0	0	0	0	0	0
	3	220	130	110	160	100	70	130	50	1, 010	1, 440	150	170	90	150	180	220	100	110	80	90	130	160	10	50
	7	300	140	110	130	100	100	110	100	2, 250	2, 610	120	170	100	150	120	150	90	120	100	120	110	150	80	90
	28	380	120	120	120	110	90	110	100	3, 820	3, 310	120	210	110	170	110	170	100	180	110	140	100	160	100	140
12	1	0	(185)	(0)	(230)	(70)	(0)	(0)	(0)	0	0	(510)	(1,260)	(0)	(0)	(730)	(1,630)	(80)	(290)	(0)	(0)	(0)	(0)	(0)	(0)
	3	250	130	90	130	90	40	100	70	750	1, 630	180	190	110	100	240	190	120	130	90	50	150	100	50	40
	7	260	160	100	140	120	90	110	90	1, 470	2, 160	160	190	120	110	160	180	130	160	110	80	140	130	110	90
	28	355	140	100	130	120	80	110	80	2, 670	3, 090	150	220	120	100	140	170	120	160	120	80	130	150	120	100

[a] At 7 minutes.
[b] These strengths are expressed as percentages of the strengths of the similar specimens without addition.
[c] Figures in parentheses are the actual strengths in pounds per square inch.

It is considered that variations of the strengths between 90 and 110 percent should be classified as not significant. A close examination of table 8 will show exceptions, but in general the effects of the added materials were as follows:

Gypsum and calcium chloride increased nearly all the strengths, both tensile and compressive, sometimes by several hundred percent at the early ages. The increases caused by calcium chloride were usually larger than those caused by gypsum.

Sugar reduced nearly all the 1-day strengths to zero. Clinker 2 was an exception. At 3 days, clinker 9 developed no strength, but only a few of the other clinkers showed a reduction and several showed an increase. At 7 and 28 days many of the strengths were increased. Notwithstanding the fact that sugar is generally considered harmful, it is apparent that in the amounts added in these tests, it did not reduce the strengths developed by the clinker pastes after the first few days.

TDA (together with the water in which it was dissolved, 0.23 percent by weight of the clinker) reduced to zero the 1-day strengths of two of the clinkers. A few of the strengths at 1 day were increased, but the majority were either unchanged or reduced by TDA. At 7 and 28 days the tendency of TDA was, with a few exceptions, to change the strengths by only small amounts.

Tannic acid reduced nearly all the 1-day strengths to zero. At 3 days many of the strengths were decreased and only a few were increased. At 7 and 28 days in the majority of cases, tannic acid had little effect on the strengths.

Calcium acetate reduced the 1-day strengths of a majority of the clinkers. In five cases the strengths were reduced to zero. However, in a few cases rather large increases in the 1-day strengths were caused by calcium acetate. At the later ages, calcium acetate increased the strengths of a majority of the clinker pastes.

Fluosilicic acid reduced nearly all the 1-day strengths to zero. Here again clinker 2 was an exception. At 3 days the majority of the strengths were reduced, but at 7 and 28 days the strengths were left unchanged or slightly increased by fluosilicic acid.

4. SUGAR SOLUBILITY AND FLOC TESTS

The results of the sugar-solubility test are reported in table 9. Although the Merriman test was designed for use with cements, i.e., clinker plus gypsum, it may be of interest to consider the effects of the additions on the clinkers in terms of the ability of the material to pass the sugar-solubility test. The highest permissible "clear point" a cement may show and pass the test is 10 ml of 0.5 N HCl. It will be seen that only three clinkers are below this limit. Gypsum lowered all the clear points sufficiently for three clinkers having high clear points to be included in the group below 10 ml of 0.5 N HCl. Calcium chloride increased the clear points of many of the clinkers, whereas TDA affected them only slightly. Tannic acid decreased nearly all the clear points by rather large amounts in some cases, and brought two clinkers having high clear points into the group having clear points of less than 10 ml of 0.5 N HCl. Triethanolamine increased most of the clear points but decreased a few, in one case sufficiently to include the clinker in the group passing the test for cement. Calcium acetate slightly increased the majority of

the clear points. Fluosilicic acid lowered all the clear points, sufficiently for six clinkers with high clear points to include them in the group having clear points of less than 10 ml of 0.5 *N* HCl. None of the materials caused the clear points of the three clinkers, No. 1, 5, and 9, to increase sufficiently to exclude them from the group passing the sugar-solubility test for cement.

TABLE 9.—*Results of Merriman sugar-solubility test on cement clinkers with and without added materials*

Clinker	Filtrate [a]	Volume of 0.5 *N* hydrochloric acid used in titration							
		No addition	Gypsum	Calcium chloride	TDA	Tannic acid	Triethanolamine	Calcium acetate	Fluosilicic acid
		ml	*ml*	*ml*	*ml*	*ml*	*ml*	*ml*	*ml*
1	Ep	2.1	2.0	1.6	1.9	1.9	2.1	1.9	1.6
	Cp	2.1	2.0	1.6	1.9	1.9	2.1	1.9	1.6
2	Ep	31	27	28	35	44	37	35	30
	Cp	40	32	37	46	58	45	44	39
3	Ep	43	38	44	42	39	45	46	4.0
	Cp	61	50	63	60	55	63	63	4.0
4	Ep	27	3.2	33	27	2.3	2.4	27	2.1
	Cp	37	3.2	46	38	2.3	2.4	38	2.1
5	Ep	2.3	2.4	2.3	2.6	1.9	2.4	2.0	1.7
	Cp	2.3	2.4	2.3	2.6	1.9	2.4	2.0	1.7
6	Ep	25	7.7	29	25	13	22	26	2.7
	Cp	36	8.7	44	36	19	32	38	2.7
7	Ep	41	34	43	42	43	42	43	31
	Cp	63	49	66	65	67	66	66	55
8	Ep	22	10.1	29	26	6.8	24	29	2.3
	Cp	33	12.4	42	38	8.2	36	43	2.7
9	Ep	2.6	2.5	2.7	2.6	2.3	2.8	2.6	1.7
	Cp	2.6	2.5	2.7	2.6	2.3	2.8	2.6	1.7
10	Ep	19	7.3	21	22	15	22	24	5.5
	Cp	25	11.3	26	26	19	30	32	7.8
11	Ep	32	7.5	38	33	24	30	34	1.8
	Cp	39	8.4	57	39	38	46	51	1.8
12	Ep	49	45	52	49	47	48	49	30
	Cp	72	65	74	71	70	70	72	47

[a] Ep, end point; Cp, clear point.

The weights of the ignited precipitates obtained in the floc tests are given in table 10 as percentages of the total weights of clinker taken. In a few determinations, part of the hardened clinker sloughed off during filtration and was included in the weight of the floc. This accounts for the high values obtained in a number of cases. In general, the added materials affected the results of the floc test only slightly.

TABLE 10.—*Results of Paul floc test of cement clinkers with and without added materials*

[Floc in percent by weight of clinker. All observed quantities of floc were "none" except for gypsum with clinkers 3, 4, 6, and 12, which were "small", and clinkers 7 and 11, which were "medium"]

Clinker	No addition	Gypsum	Sugar	Calcium chloride	TDA	Tannic acid	Triethanolanine	Calcium acetate	Fluosilicic acid
	%	%	%	%	%	%	%	%	%
1	0.1	0.5	0.1	0.2	0.2	0.8	0.3	0.3	0.1
2	.3	.3	.4	.7	.4	.2	.6	.4	.2
3	.1	.3	.1	.2	.3	[a] 1.0	.3	.3	.1
4	.1	.2	.2	.3	.2	0.3	.2	.2	.1
5	.2	.2	.2	.2	.2	.2	.2	.1	.1
6	.1	.5	.2	.2	.2	.3	.3	.2	.2
7	.2	2.4	[a] 10.0	.5	.7	[a] 7.6	.9	[a] 2.1	[a] 7.7
8	.3	0.3	0.3	.3	.3	0.3	.3	0.2	0.3
9	.3	.3	.3	.3	.3	.3	.3	.3	.2
10	.2	.2	.2	.2	.2	.2	.2	.2	.2
11	.2	1.3	.3	.3	.3	[a] 4.8	.3	.2	[a] 3.0
12	.4	0.7	.4	.4	.3	[a] 4.7	.3	.3	0.5

[a] Particles of clinker included in weight of floc.

V. SUMMARY

The effects of added materials on 12 commercial portland cement clinkers were studied by comparing the results of tests of clinker samples containing the various additions with the results of identical tests of the clinkers alone. Determinations were made of (1) the temperature changes of the clinker pastes during one or more days after mixing, (2) the heats of hydration of the clinkers, (3) the tensile and compressive strengths of mortars and the compressive strengths of concretes, (4) the consistencies of concretes, (5) the sugar solubilities of the clinkers according to Merriman's method, and (6) the amounts of floc developed by the clinkers according to Paul's test. The materials added were gypsum, sugar (sucrose), calcium chloride, TDA, tannic acid, triethanolamine, calcium acetate, and fluosilicic acid.

It was found, in general, that while the added materials sometimes caused marked changes in the behavior of the clinker pastes during their early history, these changes were practically negligible at 28 days.

VI. REFERENCES

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